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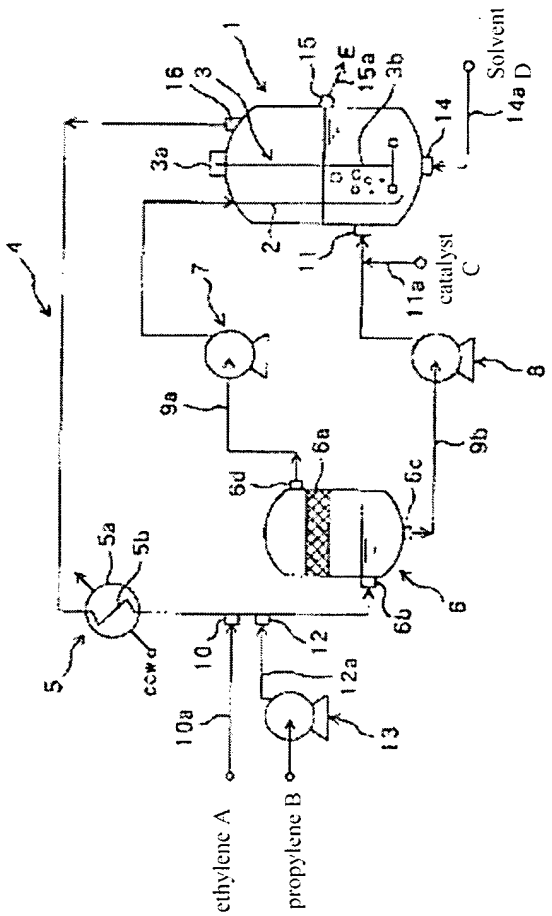
(54) TITLE OF INVENTION
Polymerizing Apparatus and Polymerizing Method

(57) ABSTRACT
PURPOSE
To provide a polymerizing apparatus which prevents high ethylene content insoluble polymer from forming during polymerization, and which can maintain the uniform polymerization reaction in a polymerizing reactor and can efficiently perform a polymer reaction.

RESOLUTION MEANS
A polymerizing apparatus having a polymerizing reactor 1 which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharge pipe 4 which removes the vapor phase from the polymerizing reactor 1, a heat exchanger 5 which removes the heat of polymerization and cools the removed vapor phase, a vapor-liquid separator 6 which separates the vapor phase which does not condense and the condensed liquid which was condensed from the removed vapor phase by the heat exchanger 5 and supply devices 9a, blower 7 which returns the condensate and the vapor which did not condense into a liquid back to the polymerizing equipment, wherein one of the supply ports 10 which supplies new ethylene A is established between the discharge pipe 4 and the vapor liquid separator 6.



SCOPE OF PATENT CLAIMS

Claim 1

A polymerizing apparatus having a polymerizing reactor which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharge plumbing which removes the vapor phase from the polymerizing reactor, a heat exchanger which removes the heat of polymerization and cools the removed vapor phase, a vapor-liquid separator which separates the vapor phase which does not condense and the condensed liquid which was condensed from the removed vapor phase by the heat exchanger, and a supply device which returns the condensate and the vapor which did not condense into a liquid back to the polymerizing equipment,

wherein one of the supply ports which supplies new ethylene A is established between the discharge pipe and the vapor liquid separator.

Claim 2

The polymerizing apparatus according to claim 1, wherein the ethylene supply port which supplies new ethylene to the polymerizing reactor is at a position lower than the liquid level of the vapor liquid separator.

Claim 3

The polymerizing apparatus according to claim 2, wherein over 50 percent of the total supply of new ethylene supplied to the polymerizing reactor is supplied from said ethylene supply port.

Claim 4

A polymerizing method comprising the steps of polymerizing ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharging the vapor phase which has not polymerized from the polymerizing reactor and cooling the discharged vapor, separating the condensate which condensed from the discharged vapor phase and the vapor phase which did not condense, and returning both the condensed condensate and the uncondensed vapor to the polymerizing reactor, wherein the aforementioned polymerizing method is also comprising a mixing processes wherein at least part of the new ethylene provided to the polymerizing reactor is mixed in a mixing process until the vapor phase which was discharged is separated into a condensate and a uncondensed vapor phase.

Claim 5

The aforementioned polymerization method according to claim 4 wherein at least part of the new ethylene supplied to the polymerizing reactor accounts for over 50% of the total amount of new ethylene supplied to the reacting apparatus.

DETAILED DESCRIPTION OF THE INVENTION

0001

TECHNICAL FIELD OF THE INVENTION

This invention relates to a polymerizing apparatus and polymerizing method having a polymerizing reactor which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid in the presence of ethylene, α-olefin, and a polymerizing catalyst.

0002

PRIOR ART

A polymerizing apparatus exists which has a polymerizing reactor which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharge plumbing which removes the vapor phase from the polymerizing

reactor, a heat exchanger which removes the heat of polymerization and cools the removed vapor phase, a vapor-liquid separator which separates the vapor phase which does not condense and the condensed liquid which was condensed from the removed vapor phase by the heat exchanger, and a supply device which returns the condensate and the vapor which did not condense into a liquid back to the polymerizing equipment.

0003
For instance, the polymerizing equipment shown in Fig. 2 is comprising a polymerizing reactor 1 which has a polymerizing reactor 3 and which polymerizes an ethylene - α-olefin copolymer in a solution, a gas spray nozzle 2 which supplies gases such as raw material ethylene A and propylene B to the polymerizing reactor 1, plumbing device 4 which sends the vapor phase from the polymerizing reactor 1 to outside of the polymerizing reactor 1, heat exchanger 5 which removes the polymerization reaction heat and cools the discharged gas phase (mixture gas), a separating apparatus (for instance a drum) 6 which distributes the mixed gas to the condensate which condensed from cooling and to the mixed gas which did not condense (non-condensate gas), supply plumbing 9b and blower 7 which returns the non-condensate gas to the polymerizing reactor 1, and supply plumbing 9b and pump 8 which return the condensate to the polymerizing reactor 1.

0004
Furthermore, supply plumbing 9a is connected to supply pipe 10a which supplies raw material ethylene (vapor) A. Furthermore, plumbing device 4 is connected to supply pipe 12a which supplies raw material propylene (liquid) B. Note, pump 13 pumps propylene B to plumbing device 4. Furthermore, supply plumbing 9b is connected to supply pipe 11a which supplies a catalyst (such as Ziegler catalyst). Furthermore, polymerizing reactor 1 is connected to supply pipe 14a which supplies a solvent (such as hexane solvent) D.

0005
Next, the case where a more uniform polymerization is performed using the polymerization equipment shown in Fig. 2 will be described with ethylene A and propylene B as the raw materials with Ziegler catalyst C and hexane solvent D in the liquid phase of the polymerizing reactor 1.

0006
The polymerizing reactor 1 is supplied raw materials ethylene A and propylene B, uses a mixer 3 to mix and polymerize ethylene A and propylene B and produces ethylene - α-olefin copolymer (polymer solution) E in a vapor-liquid coexisting state. Note that during polymerization, polymerizing catalyst C is continuously supplied to the polymerizing reactor 1 from supply pipe 11a.

0007
In the polymerization reaction, heat of polymerization is generated, so a heat exchanger 5 is necessary as a cooling means for removing this heat. Removal of the heat of polymerization is usually performed by removing the vapor phase (mixed gas) from the polymerizing reactor 1, cooling this gas in a heat exchanger 5, and then circulating the cooled mixed gas (and condensate if some condensation occurs) back to the polymerizing reactor 1.

0008
When this type of method is used, the mixed gas is removed from polymerizing reactor 1 by plumbing device 4, cooled by heat exchanger 5, and separated using a drum 6 which separates the condensate produced during cooling and the remaining non-condensate gas.

0009
Furthermore, supply plumbing 9a removes the non-condensate gas from the top of drum 6 using the

negative pressure from blower 7, and blows the uncondensed gas through the gas blowing nozzle 2 into the polymerizing reactor 1 using the forced air from blower 7.

0010
On one hand, supply plumbing 9b removes condensate (including the polymer solution, hexane solvent D, and raw material propylene B from the bottom of drum 6 using the negative pressure of pump 8 and pumps the condensate to polymerizing reactor 1 by the discharge pressure of the pump 8.

0011
By removing the mixed gas out from polymerizing reactor 1, cooling, and re-circulating back, continuous polymerization can be performed while removing the heat of polymerization generated in the polymerizing reactor 1.

0012
PROBLEM TO BE RESOLVED BY INVENTION
Incidentally, ethylene A (vapor) supplied from the gas spray nozzle 2 of polymerizing reactor 1 is dispersed as bubbles by the mixer or the like and absorbed and dissolved into the liquid phase, and while dispersed in the liquid phase, is provided and consumed in polymerization by contact with the catalyst which is the activated species.

0013
At this time, the concentration of ethylene in the liquid is preferably constant at any position in the polymerizing reactor 1. However, the dispersion speed of the ethylene which exists as vapor bubbles is relatively slow compared to the dispersion speed of ethylene which is dissolved in the liquid, so a situation tends to occur where a high concentration of ethylene exists in the liquid phase in the region around the gas spray nozzle 2.

0014
In this region of high ethylene concentration, a polymer with a high ethylene content (such as homopolymer) will be produced, and this high ethylene content polymer will have poor solubility with the ethylene - α-olefin copolymer which is the target product, so contamination of the product, known as gelling will tend to occur.

0015
In particular, when highly active metallocene is used as the catalyst, ethylene homopolymer will be quickly produced in the boundary region of the ethylene gas bubbles separated from the gas spray nozzle 2 and a large amount of insoluble polymer will be produced which is the cause of fisheye.

0016
Furthermore, in order to control the production of insoluble polymer, methods are known where the production quantity of the polymerizing reactor 1 is reduced and the dispersion rate of the ethylene is increased. However, there is a problem that this reduces the production levels.

0017
With the foregoing in view, and objective of this invention is to provide a polymerizing apparatus and a polymerizing method which can hinder the generation of high ethylene content insoluble polymer during polymerization and can uniformly and efficiently perform a polymerization reaction inside the polymerizing reactor.

0018

MEANS TO RESOLVE PROBLEMS

In order to resolve these problems, the polymerizing apparatus of This invention is a polymerizing apparatus having a polymerizing reactor which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharge plumbing which removes the vapor phase from the polymerizing reactor, a heat exchanger which removes the heat of polymerization and cools the removed vapor phase, a vapor-liquid separator which separates the vapor phase which does not condense and the condensed liquid which was condensed from the removed vapor phase by the heat exchanger, and supply device which returns the condensate and the vapor which did not condense into a liquid back to the polymerizing equipment, wherein one of the supply ports which supplies new ethylene A is established between the discharge pipe and the vapor liquid separator.

0019

Furthermore, the polymerization method of this invention is a polymerizing method comprising the steps of polymerizing ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharging the vapor phase which has not polymerized from the polymerizing reactor and cooling the discharged vapor, separating the condensate which condensed from the discharged vapor phase and the vapor phase which did not condense, and returning both the condensed condensate and the uncondensed vapor to the polymerizing reactor, wherein the aforementioned polymerizing method is also comprising a mixing processes wherein at least part of the new ethylene provided to the polymerizing reactor is mixed in a mixing process until the vapor phase which was discharged is separated into a condensate and a uncondensed vapor phase.

0020

By having the aforementioned constitution, this invention mixes raw material ethylene with the aforementioned vapor phase and brings into contact with the condensate after cooling by the heat exchanger, or mixes raw material ethylene into the condensate and partially dissolves the ethylene in the condensate, so that the high concentration of ethylene inside the polymerizing reactor can be controlled. Therefore, this invention can minimize inconsistency in the ethylene concentration within the polymerizing reactor, can minimize inconsistency of the polymer reaction inside the polymerizing reactor, and can hinder the generation of high ethylene content insoluble polymer.

0021

IMPLEMENTATION FORM OF THE INVENTION

The implementation form of the polymerizing apparatus of this invention will be described while referring to Fig. 1. First, the construction of the polymerizing apparatus of this invention will be described.

0022

As shown in Fig. 1, the polymerizing apparatus of this invention has a polymerizing reactor 1 which polymerizes ethylene and α-olefin copolymer in the presence of both vapor and liquid phases in the presence of ethylene, α-olefin, and a polymerizing catalyst, discharge plumbing 4 which removes the vapor phase (mixed gas) from the polymerizing reactor 1, a heat exchanger 5 which removes the heat of polymerization and cools the removed vapor phase, a vapor-liquid separator (such as a drum) 6 which separates the vapor phase which does not condense (non-condensing) and the condensed liquid which was condensed from the removed vapor phase by the heat exchanger 5, and a supply device which returns the condensate and the vapor which did not condense into a liquid back to the polymerizing equipment 1.

0023
Furthermore, polymerizing reactor 1 has a gas spray nozzle 2 which supplies the uncondensed gas including raw material ethylene A (vapor) into the chamber and a mixer 3 which mixes the liquid phase inside the chamber. Note, the supply tip of the gas spray nozzle 2 is established in the liquid phase near the bottom of the polymerizing reactor 1.

0024
Furthermore, polymerizing reactor 1 has a supply port 11 and a supply port 14 established in the bottom, a discharge port 15 established in the sidewall in the center region, and a discharge port 16 established in the top. Note, supply port 11 is connected to supply pipe 11a which supplies a catalyst (such as metallocene) C. Furthermore, supply port 14 is connected to supply pipe 14a which supplies a solvent (such as hexane) D. Furthermore, discharge port 15 is connected to discharge pipe 15a which discharges a polymer solution in solvent (such as ethylene - α-olefin copolymer) E. Furthermore, discharge port 16 is connected to plumbing device 4 which discharges mixed gas.

0025
Furthermore, the mixer 3 has a motor 3a and an impeller 3b connected to the shaft of the motor 3a. Furthermore, plumbing device 4 has plumbing connected from the discharge port 16 of the polymerizing reactor 1 to the drum 6 through the heat exchanger.

0026
Furthermore, supply port 10 and supply port 12 are established in the plumbing which is connected from the discharge port 16 through the heat exchanger 5 to the drum 6. This supply port 10 is connected to supply pipe 10a which supplies raw material ethylene A. Furthermore, at least part of the new ethylene A supplied to the polymerizing reactor 1 is supplied from supply port 10 through supply pipe 10a. Note, the supply quantity of new ethylene A supplied from supply port 10 is preferably no less than 50% of the total quantity of new ethylene A supplied to the polymerizing reactor 1.

0027
Furthermore, supply port 12 is connected to supply pipe 12a which supplies raw material propylene B (liquid). Furthermore, heat exchanger 5 is a device to remove the heat of polymerization from the gas which passes through, such as a condenser. Any heat exchanger 5 which is able to remove the necessary quantity of heat and is able to withstand long-term use may be used, but the case of a multi-pipe heat exchanger will be described.

0028
This heat exchanger 5 is comprised of a chamber 5a through which a coolant (such as cooling water) CCW passes and a plurality of narrow tubes 5b which pass through inside this chamber 5a. Furthermore, the narrow tubes 5b of the heat exchanger 5 are connected to the plumbing of plumbing device 4.

0029
Furthermore, the drum 6 is comprised of a chamber which temporarily stores raw material and mixed gas. A filter 6a may also be provided in this chamber. Furthermore, the filter 6a has a fiber layer which removes contaminants from the raw material and mixed gas which passes through.

0030
Furthermore, the drum 6 has a supply port 6b in the sidewall of the chamber, discharge port 6c in the bottom, and discharge port 6d in the top. Furthermore, the supply port 6b is positioned lower than the level of the liquid in the drum 6. Furthermore, supply port 6b is connected to the plumbing of plumbing device 4.

0031
Furthermore, the discharge port 6c is connected to plumbing 9b of a supply device which transports condensate. Furthermore, the discharge port 6d is connected to the plumbing 9a of the supply device which transports uncondensed gas.

0032
Furthermore, the supply device is comprised of supply plumbing 9a which is connected from the discharge port 6d of the drum 6 through the blower 7 to the gas blow nozzle 2, and supply plumbing 9b which is connected from the discharge port 6c of the drum 6 through the pump 8 to the supply port 11 of the polymerizing reactor 1. Furthermore, the supply plumbing 9b is connected to the supply pipe 11a which supplies metallocene catalyst C.

0033
Furthermore, the blower 7 is an apparatus which uses a fan to provide pressure and transport a gas (uncondensed gas). The supply side and the discharge side of this blower 7 are connected to the supply plumbing 9a. Furthermore, pump 8 is a device which uses an impeller to rapidly transport a liquid (condensed liquid) to an external chamber, and an example is a centrifugal pump. The intake and output of the pump 8 are connected to the supply plumbing 9b.

0034
Next, the polymerization method using the polymerizing apparatus of this invention will be described. Note, the case will be described where uniform polymerization is performed with the polymerizing apparatus using ethylene A and propylene B for the raw material, while supplying metallocene catalyst C and hexane solvent D in the liquid phase of the polymerizing reactor 1.

0035
First, raw material ethylene A is supplied to supply port 10 of the plumbing device 4 from supply pipe 10a, while raw material propylene B is pumped by pump 13 and supplied from the supply pipe 12a to the supply port 12 of the plumbing device 4.

0036
Therefore, ethylene A and propylene B are transported to the drum 6 from supply port 6b, and are temporarily stored while being partially dissolved. Furthermore, ethylene A and propylene B are separated into a liquid phase (propylene B and polymer solution) and a vapor phase (ethylene A) in the drum 6.

0037
The uncondensed gas with ethylene A as the major component is discharged by the negative pressure of the blower 7 from discharge port 6d to the supply plumbing 9a, passes through supply plumbing 9a, is pressurized by blower 7 and supplied to polymerizing reactor 1 from the gas blower nozzle 2.

0038
The condensate with propylene B as the major component is discharged from discharge port 6c to supply plumbing 9b. The condensate in supply plumbing 9b is pumped by pump 8 and supplied from supply port 11 to the liquid phase of polymerizing reactor 1. Note, metallocene catalyst C and hexane solvent D are continuously supplied from respective supply pipes 11a, 14a to the supply ports 11, 14 for the polymerizing reactor 1. The hexane solvent D is removed from the polymerizing reactor 1 and un-reacted ethylene A and propylene B may also be included.

0039
The mixer 3 mixes the uncondensed gas and the condensate together with the metallocene catalyst C and the hexane solvent D using the impeller 3b. Note, metallocene catalyst C promotes polymerization and hexane solvent D promotes solubility. Therefore, ethylene A and propylene B are polymerized and ethylene-α-olefin copolymer E is produced in solution in the liquid phase of polymerizing reactor 1.

0040
On the other hand, evaporating gas (vapor phase) which does not stay in solution is produced in the top part of the polymerizing reactor 1 because of the heat of polymerization. This vapor phase is a mixed gas comprising ethylene A, vaporized propylene B, and vaporized hexane solvent D.

0041
Furthermore, this vapor phase (mixed gas) is discharged from the discharge port 16 to the plumbing of plumbing device 4. The discharged mixed gas is transported to the heat exchanger 5 in the plumbing of plumbing device 4, and passes through the narrow tubes 5b of the heat exchanger 5. Therefore, the heat exchanger 5 removes the heat of polymerization from the mixed gas which passes through the narrow tubes 5b by the action of the heat exchanger and the coolant CCW. Therefore, the mixed gas will partially condense and will form a vapor liquid mixture of condensate liquid and uncondensed gas.

0042
Furthermore, the cooled mixed gas (gas-liquid mixture) is mixed with ethylene A supplied from the supply port 10 and the propylene B supplied from supply port 12 of and is temporarily stored in the drum 6 from the mixed air supply port 6b. Note, this mixing process is performed until the mixed gas is separated into condensate which was condensed by cooling and the uncondensed gas. Furthermore, the ethylene A supplied from supply port 10 is mixed and cooled with the cooled mixed gas and is partially dissolved (polymerized) in the condensate in the drum 6.

0043
Therefore, drum 6 is supplied condensate (liquid with propylene B as the main component) which was condensed by cooling and uncondensed gas (mixed gas containing primarily ethylene A) which was not condensed.

0044
Therefore, the uncondensed gas is discharged from discharge port 6d to the supply plumbing 9a by the negative pressure of blower 7. Furthermore, the uncondensed gas in the supply plumbing 9a is blown by blower 7 and supplied to the polymerizing reactor 1 from the gas blow nozzle 2. Note, no less than 50% of the total supply quantity of ethylene supplied to the polymerizing reactor 1 is mixed with the cooled mixed gas, and after being partially dissolved in the condensate in drum 6, is supplied the polymerizing reactor 1 from the gas blow nozzle 2.

0045
On one hand, the condensate which is primarily propylene B is discharged from discharge port 6c to supply plumbing 9b. The condensate in supply plumbing 9b is pumped by pump 8 and supplied to the liquid phase in the polymerizing reactor 1 from the supply port 11.

0046
Therefore, the uncondensed gas which is supplied to the polymerizing reactor 1 from the gas blow nozzle 2 is a mixture of raw material ethylene A and mixed gas, so the concentration of ethylene is low compared to raw material ethylene A.

0047
Therefore, when a relatively low concentration of ethylene (in other words mixed gas) is mixed and placed in contact with the propylene B, the region of high concentration ethylene in the polymer solution is reduced, so a cause of producing insoluble polymer with high ethylene content can be removed, and therefore a more consistent polymerizing reaction in the polymerizing reactor can be obtained.

0048
In the aforementioned implementation form, the supply port 10 for the raw material ethylene A is connected to the plumbing device 4, and the raw material ethylene A is mixed and supplied with the mixed gas in the plumbing of plumbing device 4, but in another implementation form, the supply port for the raw material ethylene A is established beneath the liquid level of the drum 6, and the raw material ethylene A is mixed and supplied with the condensate in drum 6.

0049
EMBODIMENTS
This invention will be described in further detail below, by showing embodiments of this invention, but This invention is not restricted to these embodiments. Note, with the embodiments of this polymerizing apparatus, ethylene and propylene were used as raw materials, and metallocene catalyst and hexane solvent were supplied.

0050
(Embodiment 1)
With the polymerizing apparatus shown in Fig. 1, the quantity of monomer supplied (kg/h) was 3330 kg/h of ethylene and 1170 kg/h of propylene.

0051
Therefore the quantity of ethylene polymer that could be obtained was 3330 kg/h. In this case, insoluble polymer with high ethylene content did not occur. Furthermore, the rate of absorption of ethylene in the polymerizing reactor was 1360 kg/h, or 40.84% of the total ethylene polymerized quantity. Furthermore, the rate of ethylene absorption in the drum was 1970 kg/h, or 59.16% of the total ethylene polymerized quantity.

0052
(Comparison Example 1)
In the conventional polymerizing apparatus shown in Fig. 2, the quantity of monomer supplied (kg/h) was the same as embodiment 1.

0053
The rate of ethylene polymerization obtained was 3330 kg/h, but in this case, an insoluble polymer with high ethylene content was produced. Furthermore, the quantity of ethylene absorbed in the polymerizing reactor was 1710 kg/h or 51.35% of the total ethylene polymerization quantity. Furthermore, the quantity of ethylene absorbed in the drum was 1620 kg/h, or 48.65% of the total ethylene polymerization quantity.

0054
As described above, embodiment 1 suppresses the concentration of ethylene by mixing the raw material ethylene with the mixed gas in the plumbing of plumbing device 4, so insoluble polymer with high ethylene content was not produced. Furthermore, embodiment 1 suppresses the concentration of ethylene, so the polymerization rates in the polymerizing reactor 1 of embodiment 1 is lower than that of comparison example 1, but embodiment 1 has part of the raw material ethylene preliminarily dissolved in the condensate solution in the drum 6 so the rate of polymerization in the drum 6 of embodiment 1 was

higher than that of comparison example 1, so the total rate of polymerization was the same for both embodiment 1 and comparison example 1.

0055

EFFECT OF INVENTION

Because of the construction described above, this invention mixes raw material ethylene and the mixed gas, and after cooling by the heat exchanging effects of the heat exchanger, the mixture is brought in contact with the condensate, alternatively, the raw material ethylene is mixed with the condensate and partially dissolved in the condensate, so in the polymerizing reactor, the mixed gas with a concentration of ethylene lower than the raw material ethylene is brought into contact and mixed with the α-olefin composition.

0056

Therefore, This invention suppresses the concentration of ethylene below that of the raw material ethylene in the polymerizing reactor, reduces the inconsistency of the polymerizing reaction in the polymerizing reactor, and can prevent generation of an insoluble polymer with high ethylene content.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is an equipment arrangement diagram for the polymerizing equipment of this invention.
Fig. 2 is an equipment arrangement diagram for conventional polymerizing equipment.

DESCRIPTION OF FLAGS

1 ..... polymerizing reactor
2 ..... gas blow nozzle
3 ..... mixer
4 ..... plumbing device
5 ..... heat exchanger
6 ..... separating equipment (drum)
9a, 9b ..... supply device (supply plumbing)
10 ..... supply port

Fig. 1

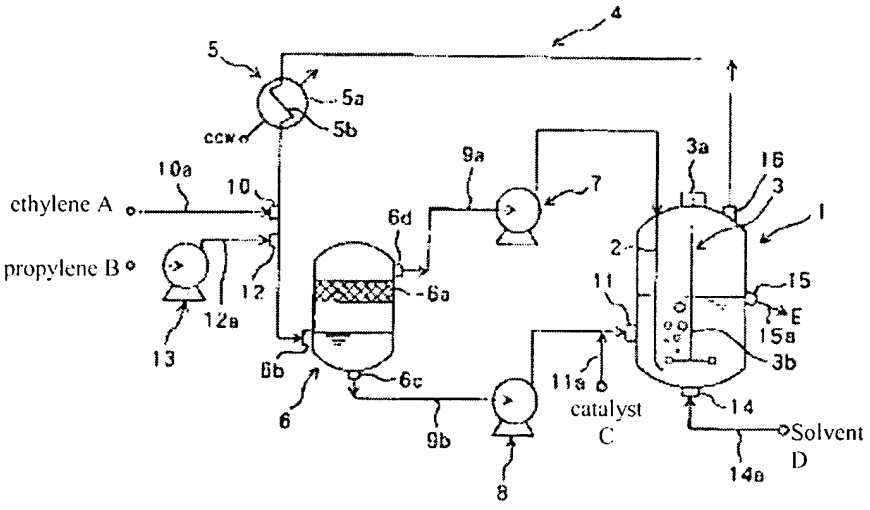
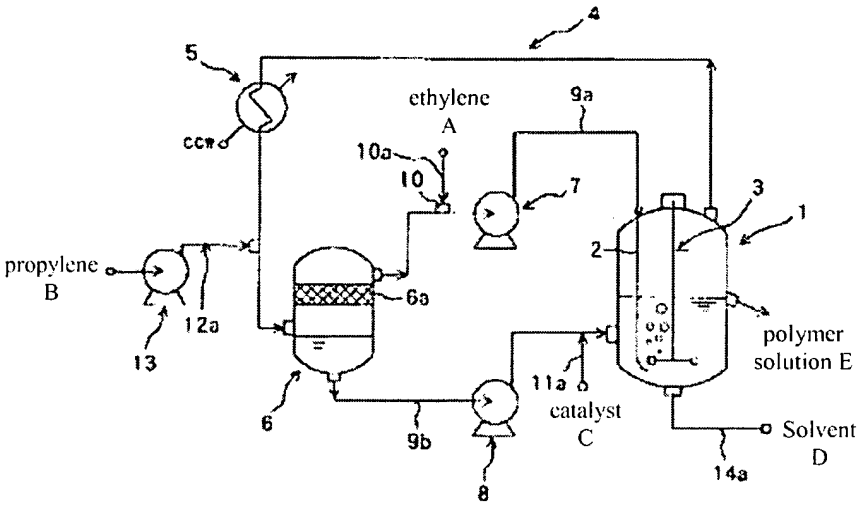


Fig. 2


4
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ccw
ethylene
A
9a
10a
10
7
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13
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solution E
11a
catalyst
C
6
9b
8
Solvent
D
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